Synthetic Organic Chemicals

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Cellulose Acetate Solvents

BEFORE discussing cellulose acetate solvents it may be well to state that the material to be dissolved is a colloid and as such gives under usual conditions collodial solutions. It may also be of interes to mention that it is possible to obtain cellulose acetate with widely varying solubility characteristics.

The factors which appear to influence the solubility in various reagents are chiefly two: acetyl content, and molecular magnitude. The former is susceptible of accurate evaluation, but as yet the latter has not been subjected to definite measurement, though many attempts have been made to ascertain the size of the colloidal particles in solutions.

If the hydroxyl groups in cellulose be fully acetylated, a product is obtained which contains 44.8% acetyl. This material is soluble in several solvents. If the cellulose triacetate be partially hydrolyzed it becomes possible to obtain a much wider variety of solvents and upon continued hydrolysis it is regenerated to cellulose in a somewhat degraded colloidal form for which no solvent has as yet been found which does not simultaneously decompose the material.

Cellulose contains three hydroxyl groups per $C_6H_{10}O_5$ unit, and as stated above, the complete esterification of these groups results in the production of cellulose triacetate, containing 44.8% acetyl. The characteristic solvent for this material is chloroform, and has led to its frequent designation in the literature as "chloroform-soluble cellulose acetate." It is also soluble in glacial acetic acid, tetrachloroethane, mixtures of ethylene dichloride or chloroform with methyl or ethyl alcohol; pyridine, hot nitrobenzene, and in warm aniline. This is by no means a complete list of solvents for cellulose triacetate, but may serve as a suggestive group of reagents to indicate the wide variety of solvents available. Certain of these solvents and solvent combinations are the subject of patents and should not, therefore, be employed upon a commercial scale without first taking into consideration the patent situation pertaining thereto.

From a technical standpoint the properties of partially hydrolyzed cellulose acetate have brought it into wide use for rayon and in making photographic films. The development of cellulose acetate lacquers has already been begun. While cellulose triacetate is practically insoluble in cold anhydrous acetone, the partial hydrolysis to an acetyl content of from 36 to 42% renders it readily soluble in this ketone and it is frequently referred to as "acetone-soluble cellulose acetate." Whereas, cellulose triacetate produces weak and brittle threads, sheets, and films, the corresponding products produced from acetone soluble acetates are strong and flexible. The low inflammability of all cellulose acetates,

being about that of paper, has led to many uses in place of cellulose nitrate with its rather higher inflammability and lower stability.

Cellulose acetate containing less than 36% acetyl is no longer soluble in acetone, but is soluble in warm 75% ethyl alcohol, and in hot aniline.

Since the preponderance of cellulose acetate available is soluble in acetone, other solvents for this material will be discussed at some length, though it will, of course, be impossible to give a complete list, and the discussion will be confined largely to types of compounds. Cellulose acetate is soluble in organic acids such as formic, acetic, and propionic acid. In the fatty acid series the solubility decreases with lengthening chain. It is soluble in esters, of which methyl acetate, methyl lactate, and glycol diacetate may be mentioned as examples.

Partially hydrolyzed cellulose acetate is soluble in other ketones than acetone, such as acetophenone and methyl ethyl ketone; however, as the length of the hydrocarbon chain increases the solubility of the cellulose acetate decreases. When the hydrocarbon chain becomes a saturated cyclic ketone, solubility is again high as evidenced by cyclohexanone, which is a good solvent for cellulose acetate of between 36 and 42% acetyl.

There are also solvents to be found among the heterocyclic compounds of which 1, 4-dioxan, tetrahydrofurfuryl alcohol, pyridine and piperidine are examples.

As mentioned under cellulose triacetate, hot aniline and hot nitrobenzol are also solvents for "acetone-soluble cellulose acetate."

Heating cellulose triacetate in boiling aniline, however, results in the removal of acety groups and the final regeneration of cellulose. Hot nitrobenzol solutions gel on cooling.

Of the halogenated hydrocarbons, tetrachloroethane is a good solvent for cellulose acetate over a wide range of acetyl content, as are mixtures of chloroform, dichloroethane, or ethylidine chloride with methyl or ethyl alcohols. Ethylene chlorhydrin is also a solvent for cellulose acetate, but its low stability with the production of hydrochloric acid requires that caution be exercised in its use. It appears that ethylene acetochlorhydrin, in which cellulose acetate is also stated to be soluble, might be more suitable from this standpoint. Dichloroethylene when mixed with alcohol dissolves cellulose acetate. Carbon tetrachloride is a non-solvent for all types of cellulose acetate thus far investigated.

While dimethyl, methyl-ethyl, diethyl ether or other ethers of this type are not solvents for cellulose acetate, the corresponding ethers of ethylene glycol, such as monomethyl or mono-ethyl ether of ethylene glycol, are solvents. The former is the better solvent for cellulose acetate. The ethers of the poly-ethylene glycols are solvents of moderate activity, while the acetates of the above ethylene glycol ethers are good solvents for cellulose acetate of between 36 and 42% acetyl.

In the carbocyclic ethers it is stated that mixtures of anisol or phenetol with alcohol are suitable solvents and that guaiacol will dissolve "acetone-soluble cellulose acetate" in the cold.

No types of cellulose acetate have as yet been produced which are soluble in either aliphatic or aromatic hydrocarbons alone, though it is mentioned in the literature that acetone soluble cellulose acetate is soluble in mixtures of hot ethyl alcohol and benzol.

While the above is by no means an exhaustive exposition concerning cellulose acetate solvents, it is hoped that in the variety and types of compounds mentioned it may serve to indicate the general solubility properties of this very interesting colloidal material.

A Convenient Laboratory Distilling Head

THE organic chemist engaged in synthetic work does not ordinarily require a great variety of apparatus, but can make a few flasks and condensers fulfill his needs. There are, however, some additional pieces of glassware, particularly in the line of distillation apparatus, which save much time and make for greater convenience. One of the simplest and most useful of these articles is the distilling head shown in Fig. I. With

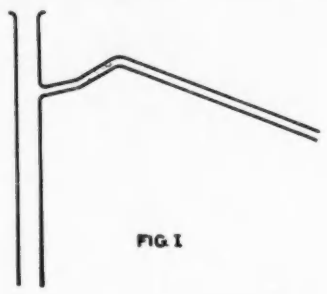
FIG. I

slight modification it can be assembled with other equipment to form several different types of laboratory distilling apparatus.

Fig. II shows the distilling head used to convert a short neck flask to a distilling flask. These heads are particularly useful when applied to flasks of a capacity of two liters or more, and wherever there is danger of breaking the ordinary

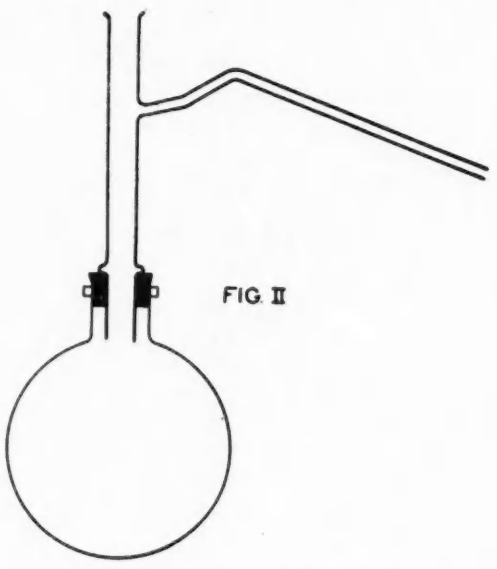
FIG. II

flask during the distillation. The shoulder shown in the diagram helps to prevent the stopper from being sucked into the flask during vacuum distillations.

A Claissen flask can be made very easily by indenting the side wall of the column and sealing it to another tube as illustrated in Fig. III. The opening

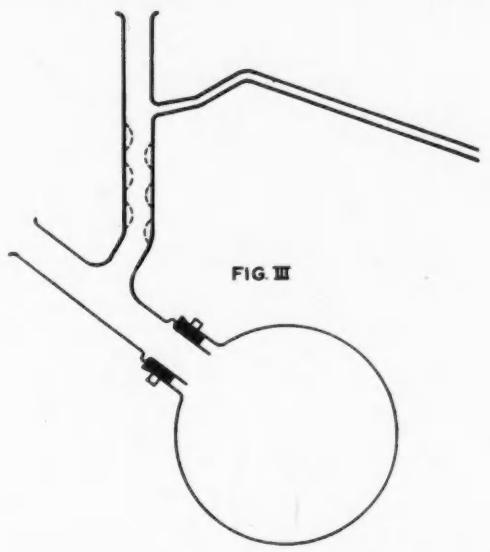
FIG. III

where the column joins the tube should be larger than the column itself. The inexperienced glass blower will find it easier to make the indentations by heating a spot in the column and sucking in the softened glass into the form of an inside bulb rather than attempting to make them with the end of a file. By tilting the main part of the flask at an angle of 45° there is much less tendency for the side-arm to fill up with the liquid carried by the vapor. In fact, in most cases it is unnecessary to add tile or a piece of capillary tubing to reduce the bumping during vacuum distillations. The humped side-arm nearly eliminates contamination from the stopper unless the distillation is carried on too rapidly.

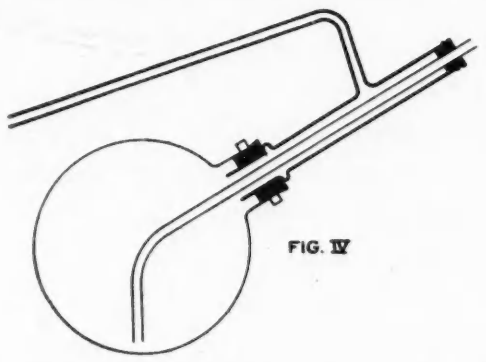
FIG. IV

The distilling head is easily converted to a steam distillation set-up by adding

an inner tubing for the introduction of steam as shown in Fig. IV. The length of tube can be adjusted to fit flasks of any size. The ease of fabrication and many uses of this simple piece of glassware make it desirable to have a number of them available in the organic laboratory.

Organic Chemicals as Analytical Reagents

X. REAGENTS FOR GOLD

FORMALDEHYDE

Muller and Foix, B. Soc. Chim. *31*, 717 (1922)

The reduction of gold salts to a colloidal form takes place when a dilute alkaline solution of a gold salt is treated with formaldehyde. The blue color is then compared with known standards. The optimum concentration for the determination is one part in 40,000. Forty cc. of the solution (containing approximately 1 mg. of gold) is treated with 1 cc. of 20% sodium hydroxide and 1 cc. of 40% formaldehyde. Other reducible metals must be removed previous to the determination.

PHENYLHYDRAZINE

Pozzi-Escot, Ann. Chim. Anal. *12*, 90 (1907)

The presence of gold in minerals can be determined by the blue-violet color obtained by adding phenylhydrazine to a solution of the mineral. The finely powdered mineral is treated for a time with chlorine water, and the filtered solution boiled to expel the chlorine. About 25 cc. of the solution is acidified with formic or citric acid and a few drops of phenylhydrazine hydrochloride solution added. The intensity of the color by transmitted light is roughly proportional to the amount of gold present.

BENZIDINE

Malatesta and di Nola, B. Chim. Farm. *52*, 461 (1912)

Traces of gold as low as 2 parts per million can be detected by the use of benzidine. The reagent consists of 1 gram of benzidine in 10 cc. of acetic acid and 50 cc. of water. With traces of gold in solution an intense blue coloration is formed. Iron salts give a similar color and platinum yields a blue flocculent precipitate. These metals must, therefore, be removed before the test.

o–TOLIDINE

Pollard, Analyst *44*, 94 (1919)

One gram of o-tolidine dissolved in a liter of 10% hydrochloric acid can be used as a test for gold chloride. One part of gold in a million parts of water gives a bright yellow color upon addition of one cc. of this reagent. The principal interfering substances are free chlorine, nitrous acid, and ferric iron. The reduction of the gold by impurities in reagents should also be guarded against.

m–PHENYLENEDIAMINE

Siemssen, Chem. Zeit. *36*, 934 (1912)

A 0.5% solution of gold chloride when treated with a 0.5% solution of m-phenylenediamine sulfate gives a yellow or brownish color due to the formation of colloidal gold. With more dilute solutions the color changes to a violet hue. Solutions of the reagent which have become colored from exposure to air or light may be purified by boiling with animal charcoal.

New Chemicals

The following new chemicals have been added to our stock since the publication of List No. 20:

*Dicaprylamine
*4–Dihydroxyethylamino–1–hydroxybenzene
*Diphenylanisyl Carbinol
p–Nitrodiphenyl
*N–Nitroso–N–ethylurethane

*Made or purified in the Kodak Research Laboratories.

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Organic Chemicals as Plant Stimulants

THE effect of various organic chemicals on plant growth has attracted a great deal of attention in recent years. Not only botanists and fruit growers, but the general public have been interested in the results of experiments along these lines. The citrus fruit-growers and packers had realized that American buyers were "color conscious" long before this fact was recognized by manufacturers of automobiles, cameras, fountain pens and plumbing fixtures. Regardless of the fact that the color of citrus fruit quite often gives little indication of the taste or food value, it is almost impossible to sell green-colored lemons or oranges. The housewife insists on the bright yellow or orange color which is so often associated with ripeness.

Fruit growers had found that the desired change in color could be brought about by burning kerosene in stoves scattered throughout the storage rooms. The products of combustion of the kerosene helped to decolorize the green pigment, and thus make the fruit acceptable at the markets. The U. S. Bureau of Chemistry, in conducting experiments to determine the effective agent in this empirical process, found that small amounts of ethylene would produce the necessary color change. As a result of their work, carload lots of oranges, lemons and grapefruit can be treated with ethylene gas, either in tents or easily ventilated rooms, and thus given the color desired for table use.

The time required for coloration varies with the original color, temperature, method of packing, etc. Under commercial conditions about one cubic foot of ethylene per 1,000 cubic feet of space is used, but under laboratory conditions, as little as one part of ethylene mixed with 10,000 or 100,000 parts of air will bring the fruit to the proper color. As near as can be found, the treatment has no deleterious effect on the sugar content or other characteristics of the edible portions of the fruit. Apparently, the ethylene does not combine with the green pigment to produce the change in color directly, but it is by the stimulation of the life activity of the fruit that the decoloration is brought about.

A great deal of this work at the Bureau of Chemistry was carried on by Dr. F. E. Denny, who later continued the study of the effect of chemicals on plant growth at the Boyce Thompson Institute for Plant Research. The experimental work carried on there during the last few years on shortening the rest period of plants has shown striking results.

As most people who are interested in gardening know, there are many perennial shrubs, plants and trees which do not appear to have a continuous growth. Many of these plants and bulbs go into a dormant state during which the regulation of temperature and moisture to the most favorable conditions seems to have little effect. For instance, well developed buds form on the lilac about the middle

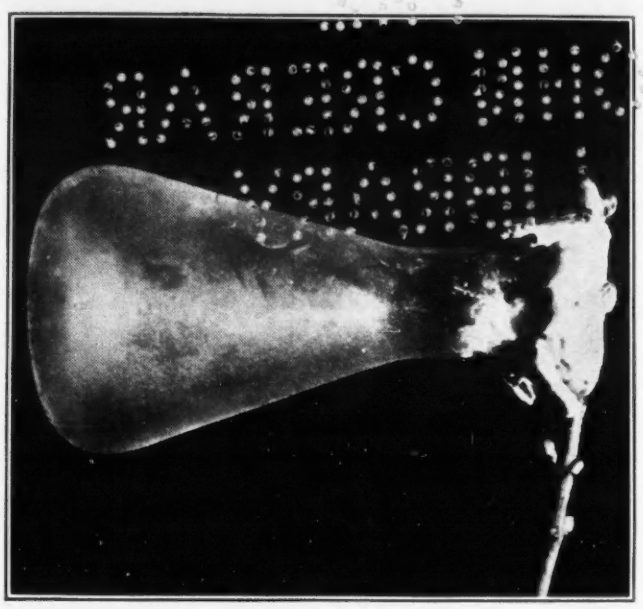


FIG. I—*Method of Treating Single Buds*

FIG. II—*Treated and Untreated Twigs on the Same Stem*

of July, yet in spite of the summer heat and rain, they do not blossom until spring. Even if brought into a greenhouse in the fall, they seldom start to bloom until February or later. Likewise, potatoes require a rest period after harvesting before they are able to start sprouting.

In places like Bermuda and some of our southern states, the climatic conditions permit the growth of two crops of potatoes. The necessity for a rest period, however, prevents using seed from the first crop for planting the second. If two crops are to be planted, it is necessary to hold the seed over in cold storage from the previous year, or to use seed from early potatoes grown in northern states especially for this purpose.

Subsequent to the pioneer investigations of Johannsen in Denmark, experimental work on stimulating the growth of dormant plants by chemical means was done by state agricultural experiment stations and by various independent investigators. The investigation carried on by Denny and his associates at the Boyce Thompson Institute involved the use of nearly 250 chemicals in 3,000 individual experiments. As a result of this work, it was found that the rest period of some varieties of potatoes could be reduced by as much as two months. Lilacs and flowering almonds were forced into blossoming by Christmas, indicating that many more blooming plants may soon be obtainable during the holiday season.

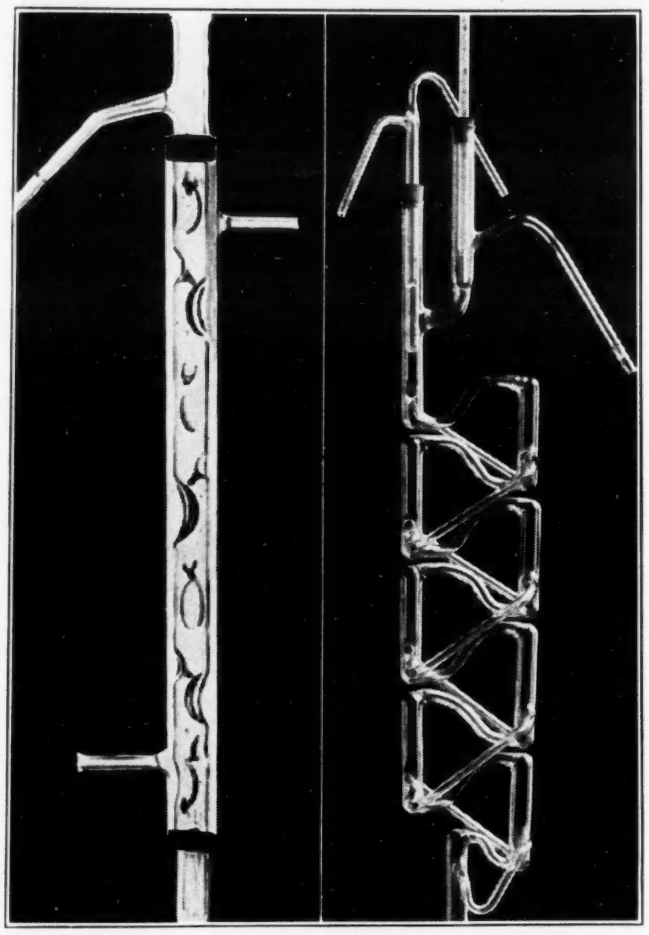
Ethylene chlorhydrin was found to be one of the most effective agents, although many others, such as sodium thiocyanate, thiourea, ethylene dichloride, furfural, ethyl bromide and vinyl chloride were also effective. In the "chlorhydrin dip" method, the cut potatoes were dipped in a solution containing 30 cc. of 40% ethylene chlorhydrin and 970 cc. of water, after which they were stored in closed containers for 24 hours. During this period, in which the vapors were acting on the buds, it was found necessary to keep the temperature below 32° C. to prevent injuring the seed pieces.

The method of treating individual lilac buds with the vapors of organic chemicals is shown in Figure I, where a flask is attached to the twig with moulding clay. In Figure II, the left-hand branch of a pair of lilac twigs was treated with ethylene chloride vapors. This shows the astonishing rate of growth as compared with the untreated twig on the right.

Both of the photographs on this page are reproduced through the courtesy of Dr. Denny.

Efficient Fractionating Columns for the Laboratory

THE rapidity with which the separation of most organic liquids can be made by distillation depends very much on the efficiency of the fractionating column used. Consequently, numerous types have been suggested as improvements over the straight-tube distilling head. In addition to its efficiency, the choice of a distilling column for an industrial laboratory depends on its simplicity, ruggedness and freedom from tendencies which may interrupt the distillation. The two columns shown in the photographs on this page possess some of these desired qualities, and are used much more than any of the other types in the preparation of our chemicals.



The column on the left is made from two pieces of straight tubing, the inner one of which has a series of indentations which increase the condensing surface. The indentations are easily formed by heating the tube in one spot and sucking in the glass at that point. Small baffles which lead the reflux over these indentations, may be made by inserting the point of a file in the softened glass at the positions shown in the photograph. The increased surface and the deflected path of the vapor makes this type much more efficient than the ordinary straight distilling head. The temperature of the column may be regulated by the rate of flow of air or water through the jacket.

The second fractionating column shown is even more efficient, and also a trifle more complicated to make. Its construction is, however, less difficult than the appearance would indicate, and its applicability to many difficult separations makes it very valuable. It consists of a series of traps joined together in such a way that the vapor ascending in each is bubbled through a 2-3 mm. layer of the refluxing liquid. Any excess condensate passes through an outlet tube to the trap below. The rate of refluxing can be controlled by adjusting the length of the water-cooled condenser which is inserted in the top of the column. This type of column holds back more of the distillate than some others, but it is easily recovered by rocking the column from side to side a few times. This minor disadvantage is more than offset by the fact that the refluxing liquid does not fall back into the boiling flask if the distillation is halted temporarily.

The constructional details of this "bubbler" type column are given in a paper by Clarke and Rahrs, in Ind. & Eng. Chem. *18*, 1092 (1926).

Organic Chemicals as Analytical Reagents

XI. REAGENTS FOR LEAD

AMMONIUM THIOCYANATE-PYRIDINE

Spacu and Dick, Z. Anal. Chem. *72*, 289 (1927)

A rapid method for the determination of lead is based on the formation of the difficultly soluble Pb(OH)SCN. To 50 cc. of the solution to be analyzed, which should contain not more than 0.3 g. of lead, are added, with stirring, 2 g. of ammonium thiocyanate and 1 cc. of pyridine in a few cc. of water. The white precipitate is filtered through a Gooch crucible and washed; first with dilute pyridine and thiocyanate solution, then alcohol, and finally ether. After drying in a vacuum dessicator for 10 minutes, the precipitate containing 73.4% Pb can be weighed.

s–DIPHENYLCARBAZIDE

Yoe, Photometric Chemical Analysis p. 255 (1928)

This is an indirect colorimetric method in which the lead is precipitated as chromate by addition to a known amount of potassium dichromate solution. After filtering off the lead chromate, the unused dichromate is determined in the filtrate, from which the amount precipitated as lead chromate can be calculated. The chromate is determined by the depth of the violet coloration produced upon addition of an acetic acid solution of s-diphenylcarbazide.

ANILINE

Morgan, Ind. & Eng. Chem. *11*, 1055 (1919)

Lead dioxide in the presence of litharge can be determined by its oxidizing action on aniline, forming aniline purple. A five-gram sample is boiled for one minute with a solution containing 2 g. of aniline hydrochloride dissolved in 10 cc. of water and 5 cc. of concentrated hydrochloric acid. After cooling and filtering, the colored filtrate is compared with known standards treated in the same manner. The method is applicable in general to the determination of any oxidizing agent when it occurs as an impurity in non-oxidizing agents.

TETRAMETHYLDIAMINODIPHENYLMETHANE

Klostermann, C. A. *21*, 933 (1927)

This method was developed for determining small amounts of lead in biological material. After removal of other metals, the lead in the form of its sulfide is treated with fuming nitric acid and evaporated to dryness. The residue is oxidized with hypochlorite or bromine to lead dioxide and filtered. Colorimetric estimation of the PbO_2 is accomplished by the above reagent which on oxidation gives a blue coloration which can be compared with known standards.

New Chemicals

The following new chemicals were added to our list during the summer months:

Iso-Butyl Chloride
β–Chloroanthraquinone (Pract.)
Cyclopentanone
Ethyl Cyclopentanone Carboxylate
*Ethyl Ethyl Carbamate
Guaiacol Carbonate (Pract.)
*Histamine Hydrochloride
*α–Hydrindone
Indolepropionic Acid
Maleic Acid (Tech.)
Methylene Dianiline (Pract.)
*l–Proline
*1.1.2–Tribromoethane

*—*Made or purified in the Kodak Research Laboratories.*